THE IONIZATION OF HCl BY ELECTRON IMPACTS

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ABSTRACT

Ionization of HCl.—Current-voltage curves obtained by means of a two electrode, hot cathode discharge tube indicate ionization in stagnant HCl gas at 14 volts in agreement with the value of the ionizing potential reported by previous observers. Spectrograms showed no hydrogen lines at voltages near the ionizing potential, but they appeared faintly at higher voltages along with some bands. A considerable amount of dissociation of the gas was observed, and this was shown to be due to thermal action at the filament rather than to the discharge. The presence of dissociation products made the interpretation of the critical potential doubtful, and so the apparatus was modified to eliminate these from the region of observation. With HCl flowing continuously through a three element discharge tube in such a way that it passed through the observation chamber, where the electron impacts occurred, before it reached the filament, no hydrogen lines appeared at accelerating voltages up to 120 volts. Current-voltage curves again show a *critical potential* at 14 volts which is attributed to the ionization of the molecule without dissociation. No *band spectra* of wave-lengths between 6000 and 2000A accompany this excitation. Hence it is concluded that the molecule has no electron transitions involving a change of energy between 2 and 6 volts. When an HCl^+ ion is neutralized, the electron is probably bound in a single operation with the consequent radiation of energy equivalent to about 14 volts.

Effect of HCl on a tungsten filament.—The conductivity was observed to increase 10 percent in 5 hr. Langmuir suggests that WCl_6 formed at the cooler ends is dissociated at the hot section.

THE ionization potential of HCl has been measured by Foote and Mohler,[1] by Knipping,[2] and by Mackay.[3] These observers agree on the numerical value of the ionizing potential, but disagree in their interpretation of the process of ionization. Foote and Mohler report 14 volts and suggest that it corresponds to the dissociation of the HCl molecule into a positive hydrogen ion and a negative chlorine ion. This interpretation is based upon the fact that the work involved in the production of these ions from the molecule, which can be computed from known heats of reaction, is equivalent to 13.7 volts. Mackay reports 13.8 volts for the ionizing potential but finds no evidence of dissociation and concludes that the process involves simply the removal of one electron from the molecule. He used a modified Lenard method of

[1] Foote and Mohler, Amer. Chem. Soc. Jour. **42,** 1832 (1920).
[2] Knipping, Zeits. f. Phys. **7,** 328 (1921).
[3] Mackay, Phil. Mag. **46,** 828 (1923) and Phys. Rev. **23,** 553 (1924).

measurement[4] employing a photo-electric source of electrons and thus eliminating thermal dissociation of the molecule. We find that the latter point of view is confirmed by a spectroscopic study of the impact region when HCl is subjected to an intense electronic bombardment.

METHOD

In the early experiments of this investigation, HCl was generated by dropping concentrated H_2SO_4 on pure NH_4Cl, dried by passing over P_2O_5 and admitted at pressures of 0.01 to 0.2 mm into a simple two electrode discharge tube. The cathode was a 12 mil (0.3 mm) tungsten spiral, and the anode a platinum plate. The minimum voltages at which an arc could be struck and maintained were determined under varying conditions of pressure and filament temperature. As ionization is essential for the striking and maintaining of an arc, this minimum voltage is the ionizing potential of the gas unless ionization by cumulative action occurs, and it apparently did not occur in our experiments. The results obtained are in agreement with the value of the ionizing potential reported by the previous observers. Spectrograms were taken of these arcs in HCl with glass and quartz spectrographs, and these were examined especially for the Balmer lines of hydrogen which should appear if H^+ ions are found in any appreciable concentration in the region of the arc or if hydrogen gas is present in appreciable amount.

The appearance of $H\beta$ on the plates and the gradual accumulation of a gas not condensible at the temperature of liquid air indicated that some dissociation of the HCl had occurred. This was found to be due largely to thermal action at the filament, however. It was consequently necessary to so modify the procedure as to eliminate as far as possible the effects of these decomposition products from our observations. This was accomplished by employing an apparatus arranged as shown in Fig. 1, in which diffusion of gases from the neighborhood of the filament into the region of observation is minimized. A molybdenum diaphram, fitting the tube closely, was inserted between the filament and the plate—about 1 mm from the former and connected to the plate by a wire. This divided the tube into two compartments and separated the filament from the region of electron impacts. A fine platinum gauze covered a small aperture in the diaphram and served as a window for the passage of the gas through the tube and of electrons from the filament. A continuous flow of HCl through the observation chamber and *towards* the cathode was maintained, the rate being controlled by a

[4] Compton and Mohler, Critical Potentials, Nat. Research Coun. Bull. 48.

special stopcock *S*, with an indicator and scale. The gas passed out of the discharge tube through an arm sealed on directly above the filament and was condensed in the second liquid air trap shown in the diagram. The pump was operated continuously during a run to take off any uncondensed gas. A field for accelerating electrons was set up between the filament and the gauze, and the electrons passing through the gauze made impacts with the HCl molecules in an equipotential region between the diaphram and plate. The radiation from this region was photographed with a small Hilger quartz spectrograph through a quartz

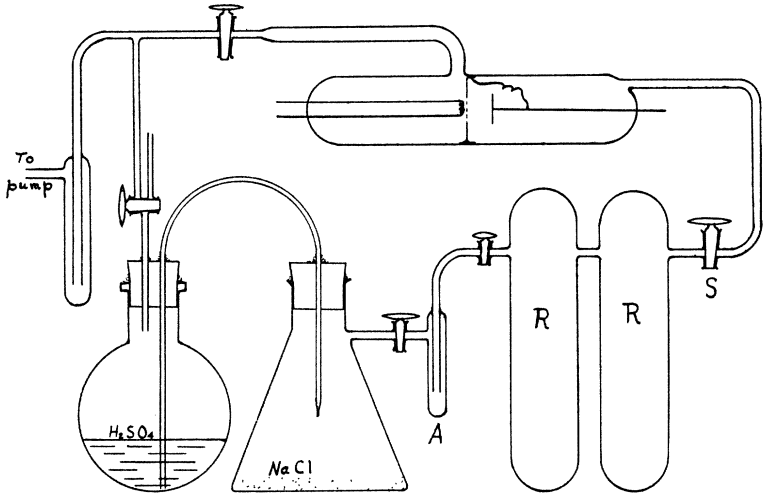

Fig. 1. Arrangement of apparatus for providing a continuous flow of HCl through the discharge tube.

window sealed on to the discharge tube, and the combined grid and plate current was measured for various accelerating voltages and gas pressures. The results indicate that the effects of dissociation at the filament and of chemical action following such dissociation were completely eliminated.

An adequate supply of HCl was prepared in advance. Concentrated H_2SO_4 and NaCl of the highest purity were introduced into the generator shown in Fig. 1 and the whole system evacuated. Then air was admitted above the H_2SO_4 in the flask causing the acid to drop slowly upon the salt. The evolved gas was collected up to atmospheric pressure in the reservoir *R*, the stopcocks closed, and the excess HCl allowed to escape through the acid flask. Liquid air was next applied to the trap *A*, condensing the HCl and any water vapor which might have

been present. The reservoir was then opened to the pump once more, and a small amount of uncondensed gas which was present was pumped off. Finally, about two-thirds of the condensed HCl was permitted to evaporate into the reservoir, the remainder being released through the generator. The gas thus collected was found to contain no detectable impurities.

Results

Typical current-voltage curves for the *stagnant gas* are shown in Fig. 2, in which the arc current is plotted against the accelerating volt-

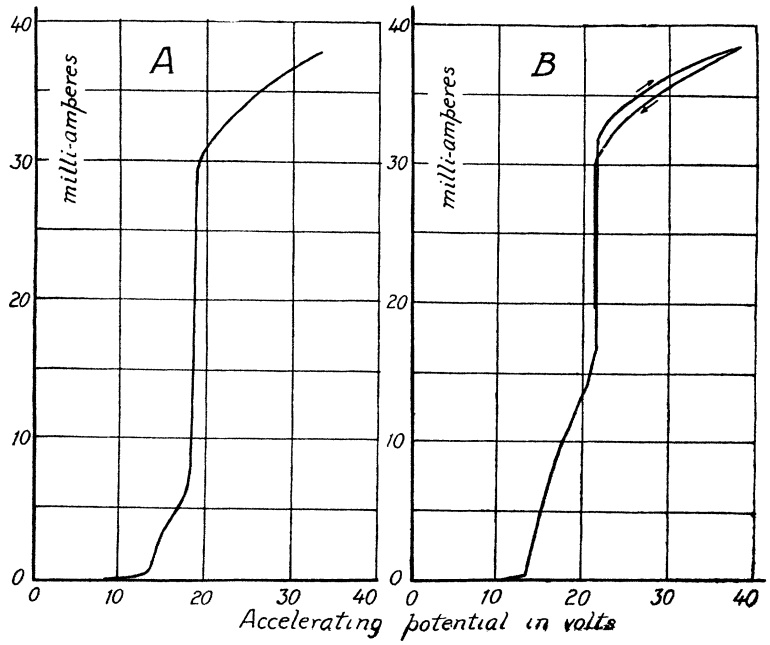

Fig. 2. Current-voltage curves in stagnant gas. The arc current in milli-amp. is plotted against the accelerating voltages. Initial pressure 0.15 mm for curve A and 0.06 mm for curve B.

age. In each an abrupt increase in current at about 14 volts is apparent, while the arc struck at somewhat higher potentials, the values of which are a function of the pressure of the gas and the temperature of the filament. The arcing potential seemed also to depend somewhat upon how long the gas had been in the tube.

The discharge was entirely colorless. At voltages above 37 the spectroscope showed Hβ faintly. Exposures of several hours at accelerating potentials up to 60 volts showed only the hydrogen lines and some

bands in the ultraviolet. These bands did not appear consistently on the plates and were probably due to accumulated reaction products, perhaps chlorine and metallic chlorides. While the tube was operating there was a noticeable clean-up of the gas, and after each run it was found that a considerable fraction of the residual gas would not condense in a liquid air trap. This must have been hydrogen, and the appearance of the Balmer lines is thus accounted for. The interpretation of the critical potential at 14 volts is in doubt, however, so long as other gases are present in the discharge tube.

Typical ionization curves obtained *with gas flowing* through the tube are shown in Figs. 3 and 4. In Fig. 3, curve *a* was obtained with no gas in the tube, and curve *b* directly afterward with a continuous flow of HCl. The arc struck at about 20 volts, but ionization set in at 14

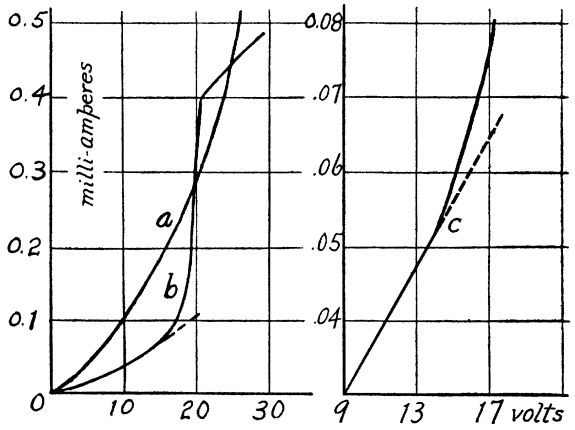

Fig. 3. Current-voltage curves. The arc current in milli-amp. is plotted against the accelerating voltages. Curve (a) without gas; (b) with HCl flowing; (c) part of curve b magnified.

volts. This is apparent from the change in curvature along a small part of this curve when plotted to a larger scale as shown in curve C. The abrupt change in slope between 13 and 14 volts is at once evident. The curve of Fig. 4 represents conditions similar to those of Fig. 3(b), and shows no other discontinuities up to 120 volts. Runs like these were made for pressures up to 0.1 mm with various filament temperatures. The average of the ionization potentials indicated is about 14 volts.

The spectrograph failed to reveal any radiation whatsoever between 6000 and 2000A when pure HCl gas flowed continuously through the apparatus. Even the Balmer lines were missing, though exposures

were made with accelerating potentials as high as 120 volts. This fact, together with the absence of deposits on the plate side of the molybdenum diaphram resulting from reactions of the gas after contact with the filament, led to the conclusion that the gauze and gas stream were effective in keeping the observation region free from impurities.

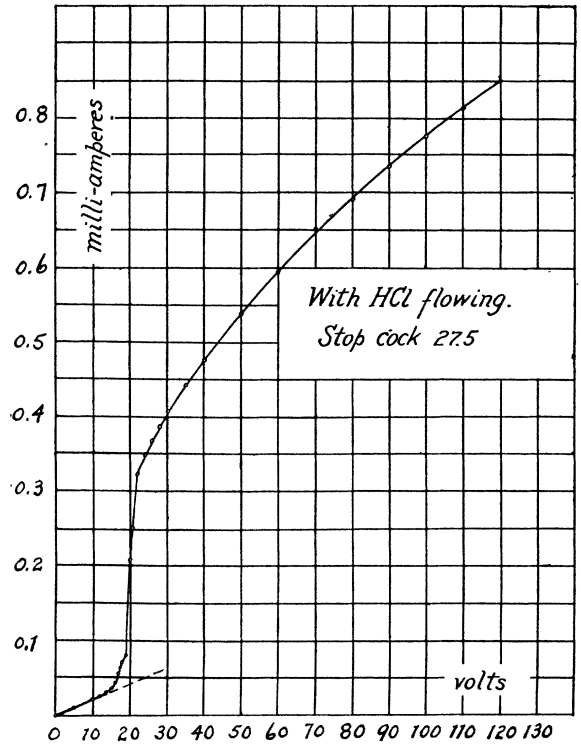

Fig. 4. Current-voltage curve for flowing gas, 0—120 volts.

The effect of the gas upon the filament is of particular interest. In Fig. 3, curves *a* and *b* were obtained with the same filament current. It will be noted that the thermionic emission for voltages below the arcing potential is very much less when gas is flowing. This is partly due to the cooling of the filament by the gas, and partly, perhaps, to a modification of the emitting surface by chemical action. The behavior of the filament in the presence of the gas was unusual in that its conductivity, instead of decreasing with use, increased throughout nearly the whole of its life. As computed from the ratio of the currents required to produce a certain potential drop across the filament, the conductivity in one instance increased over ten percent in five hours with

gas flowing at a pressure of about 0.1 mm.[5] Accompanying this action there is dissociation of the HCl, for a McLeod gauge near the mercury diffusion pump always read zero when the filament was cold and read about 0.0003 mm when the filament was hot. As the liquid air completely removed the HCl, this pressure was due to some dissociation product, undoubtedly hydrogen. The approximate rate of thermal dissociation was determined by shutting off the pump and heating the filament in stagnant gas. After 45 minutes it was found that about one-third of the gas remaining in the tube failed to condense in the liquid air trap. No increase in the amount of accumulated hydrogen was observed under similar conditions when an arc of 1.5 milli-amp. was maintained in the tube. This indicates that the amount of dissociation by electron impacts is entirely negligible compared with that produced by thermal action, and the failure of the hydrogen lines to appear supports this conclusion. The absence of dissociation in the arc implies that at the critical potential of 14 volts a molecular ion of HCl is formed.

The fact that no radiation of wave-lengths between 6000 and 2000A appears indicates that the molecule has no electron transitions involving a change of energy between 2 and 6 volts. After recapturing an electron, therefore, the normal state must be reached by a single transition, or else by combinations of steps of less than 2 and more than 6 volts. The behavior of other molecules indicates that two nearly equal steps are hardly to be expected. Also the fact that no critical potentials have been detected below that of ionization indicates the binding of the electron in a single operation with the consequent radiation of energy equivalent to about 14 volts.

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June 9, 1925.

[5] We are indebted to Dr. Langmuir of the General Electric Company for an explanation of this effect. The cooler parts of the filament are attacked by atomic chlorine from the dissociated HCl, WCl_6 being formed. This compound has a considerable vapor pressure at the temperature of the tube. The vapor is decomposed at the hot section of the filament, and metallic tungsten deposited there. The central part of the filament assumed a granular appearance after being heated in the gas due to this crystalline layer. Cf Langmuir, Amer. Chem. Soc. Jour. **37**, 1162 (1915).